Molecular Recognition in the Complexes of Dibenzo-18-Crown-6

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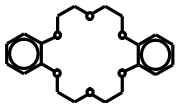

DB18C6

【Introduction】Crown ethers (CEs) can encapsulate various species by changing their conformations for the best fit. In order to elucidate the conformational preference of CEs for the complexation, we investigated the structures of jet-cooled dibenzo-18-crown-6 (DB18C6) and its complexes with water, ammonia, methanol, and acetylene. The complexes were generated by an adiabatic expansion of the gaseous mixture of DB18C6 and guest species. The electronic and IR spectra were obtained by laser induced fluorescence (LIF), and IR-UV double resonance spectroscopy, respectively.

【Results and discussion】Fig.1 shows LIF spectrum of jet-cooled DB18C6-$(H_2O)_{0\text{-}1}$.The bands labeled by **m1** and **m2** are due to the origins of different DB18C6 conformers, and the band **a** is due to DB18C6-$(H_2O)_1$. Fig.2 shows the IR spectra of species (a)**m1**, (b)**m2**, and (c)**a** in the region of the methylene CH stretching vibrations. We see that the IR spectral patterns of **m1** and **m2** are similar to each other, while that of species **a** is clearly different from them. Species **a** shows the strong band at 2830cm^{-1} but no band at 2950cm^{-1}, while those of **m1** and **m2** show opposite pattern. The spectral features imply that the DB18C6 conformation of DB18C6-$(H_2O)_1$ is different from bare DB18C6. The difference of the DB18C6 conformation was also observed in the complex with ammonia, but not with methanol or acetylene. From electronic transition energy, exciton splitting, and IR spectra of OH, NH and acetylene CH stretching vibrations, we determined the structures of DB18C6 and the complexes as shown in Fig.3. In the structures of DB18C6-H_2O and $-NH_3$, the guest molecules are incorporated in the cavity of 'boat' conformation via bidentate hydrogen-bond (H-bond). On the other hand, the DB18C6-CH_3OH and $-C_2H_2$ complexes have the same conformations of m1 and m2, respectively. The difference of the DB18C6 conformation between them can be attributed to whether the guest species can form the bidentate H-bonding with the host DB18C6.

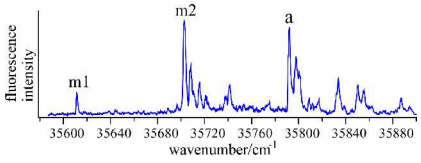

Fig.1 LIF spectrum of DB18C6-$(H_2O)_{0\text{-}1}$

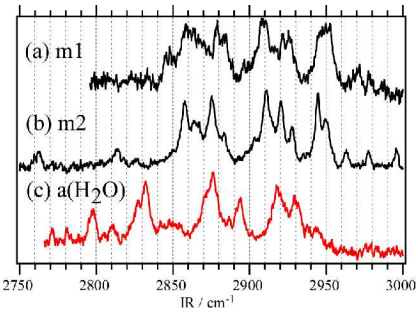

Fig.2 IR-UV double resonance spectra of DB18C6 and DB18C6-$(H_2O)_1$

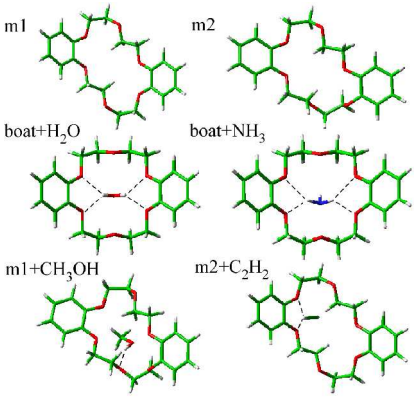

Fig.3 The most probable structures of DB18C6 and its complexes (M05-2X/6-31+G*)